AJChE 2004, Vol. 4, No. 1, 1–7

Periodic Operation of Reactive Distillation for Dehydrogenation of 2–Propanol

Shigeo Goto
Kenta Hori
Department of Chemical Engineering
Nagoya University, Nagoya 464-8603, JAPAN
Leonila C. Abella
Pag-asa D. Gaspillo
Department of Chemical Engineering
De La Salle University–Manila
2401 Taft Avenue, Manila, PHILIPPINES

The system of 2–propanol/acetone/hydrogen can be effectively provided for a chemical heat pump cycle. This research focuses on the liquid-phase dehydrogenation of 2–propanol to produce acetone and hydrogen at low temperatures under boiling conditions. The acetone produced has been known to have an inhibition effect in the liquid phase. This research examined experimentally the dehydrogenation of 2–propanol in a reactive distillation column with periodic pulse supply. The conversion of 2–propanol with periodic operation is higher than that with steady-state operation. This behavior can be explained by the acceleration of the reaction rate in the repeated vaporization steps of 2–propanol on the solid catalyst. When 2–propanol enters into the reaction part at the bottom of the column by periodic pulse, the solid catalyst repeats the wet and dry states. Thus, the resistance of mass transfer in the liquid phase and the inhibition effect of acetone both can be reduced. As a preliminary experiment, the reaction rate was measured in a batch reactor by changing the ratio of the moles of 2–propanol to the mass of solid catalyst. The optimum ratio was then found. The effect of pulse interval, feed rate, and the kind of solid catalyst on the conversion was investigated in the reactor with or without the reactive distillation part.

Keywords: Batch reactor, chemical heat pump system, enhancement ratio, liquid-phase dehydrogenation of 2–propanol, periodic operation, *and* reactive distillation.

INTRODUCTION

One of the more promising chemical heat pumps to date is the 2–propanol/acetone/hydrogen heat pump. This system can raise temperatures from about 90 to 200 °C (Saito et al. 1987, Ito et al. 1991, Kim et al. 1992, Gastauer and Prevost 1993, Taneda et al. 1993).

The basic reaction system consists of the dehydrogenation of 2–propanol in the liquid phase and the hydrogenation of acetone in the vapor phase. The dehydrogenation of 2–propanol at low temperature yields acetone

and hydrogen, where heat is absorbed due to the endothermic reaction.

$$(CH_3)_2CHOH\ (L) \rightarrow (CH_3)_2CO\ (G) + H_2\ (G) \quad \Delta H = 100.4\ \text{kJ/mol} \qquad (1)$$

This reaction is reversible and the dehydrogenation in the vapor phase is strongly limited by the equilibrium, where conversion is at 10.8% at 90°C. In the liquid phase, however, the produced acetone is a strong inhibitor due to its large amount of adsorption on the catalysts (Ito et al. 1991); hence, the dehydrogenation of 2–propanol cannot proceed.

Saito (1995) proposed to enhance the reaction rate by liquid film state on the solid catalyst in a batch reactor. Kobayasi et al. (1999) developed this idea into a spray-pulse operation on a plate catalyst.

Figure 1 compares this concept in the liquid-film state with that in the suspended state. In periodic operation, higher conversion can be expected given the acceleration of the reaction rate in the repeated vaporization steps of 2–propanol on the solid catalyst.

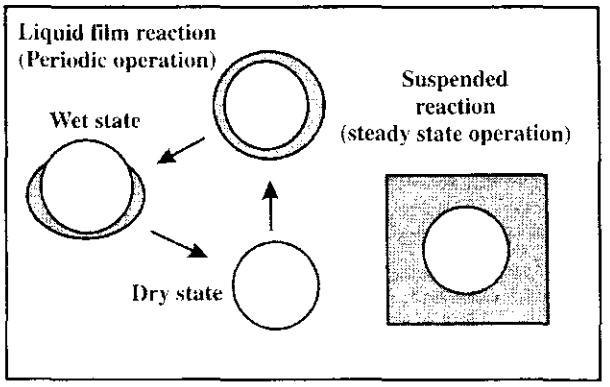

Figure 1. State of Catalyst

The aforementioned reaction had already been investigated using a reactive distillation column (Gaspillo et al. 1998). This method achieved good results.

Thus, the present study proposes to combine the methods of *periodic operation* and *reactive distillation*.

Although preliminary experiments will be carried out to check the effect of liquid volume on conversion in a batch reactor, the main objective of this study is to investigate the performance of periodic operation in varying pulse intervals, catalysts, and feed rates.

EXPERIMENTAL

Figure 2 shows the schematic diagram of the reactive distillation column. It consists of three parts, namely, the *reaction part, reactive distillation part,* and *distillation part.*

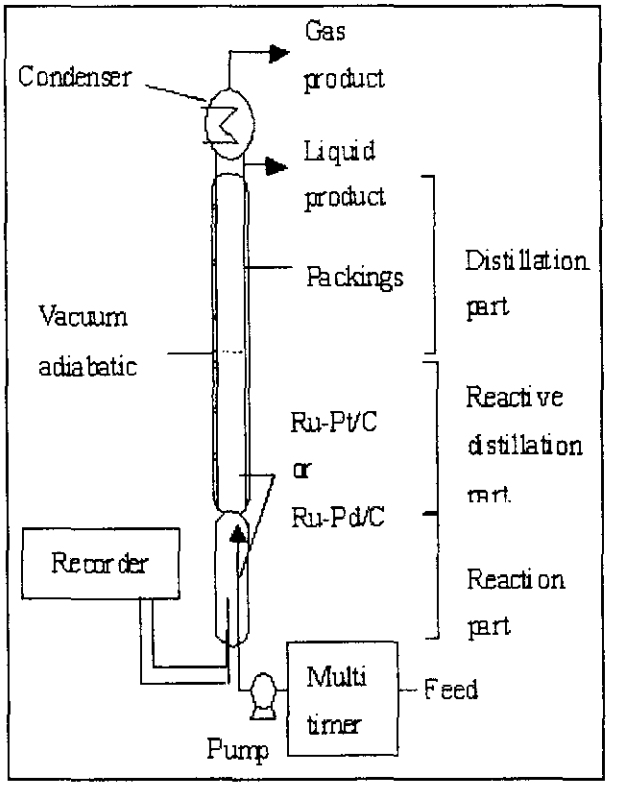

Figure 2. Experimental Apparatus

The *reaction part* consists of a column (2.5-cm in diameter and 30-cm in height) with a ribbon heater to maintain constant temperature. The 50-g catalyst was packed in the column. There were two kinds of catalysts used: (a) the composites Ru-Pt/C supported on active carbon; the weight fraction of Ru and Pt = 5 wt%, the ratio Ru/Pt = 8; and (b) the Ru-Pd/C supported on active carbon; the weight fraction of Ru and Pd = 5 wt%, the ratio Ru/Pd = 4. The cylindrical pellet was 2-mm in diameter and 3-mm in length.

Figure 3 shows the details of the reaction part. Glass pipe is inserted at the center of the column to improve heat conduction. The feed,

liquid phase 2–propanol (99.9% reagent grade), was supplied during 10 s on top of the glass pipe at the reaction part by pump. Four thermocouples were set at 14-, 17-, 21-, and 25-cm distance from the bottom.

The periodic-pulse interval was varied from 0 to 12 min, where a pulse interval of 0 min means steady-state reaction. The *feed flow rate* was determined by dividing the introduced moles of 2–proponol during pulse period with the interval period. The feed rates were adjusted at 62 and 87 μmol/s.

The column (2.5-cm in diameter and 50-cm in height) with 10 thermocouple portholes at 5-cm intervals was placed on the top of reaction part. The column was insulated with a vacuum jacket. The pressure was atmospheric.

The lower part of the column packed with 80 g of catalyst (Ru-Pt/C or Ru-Pd/C) served as the *reactive distillation part.*

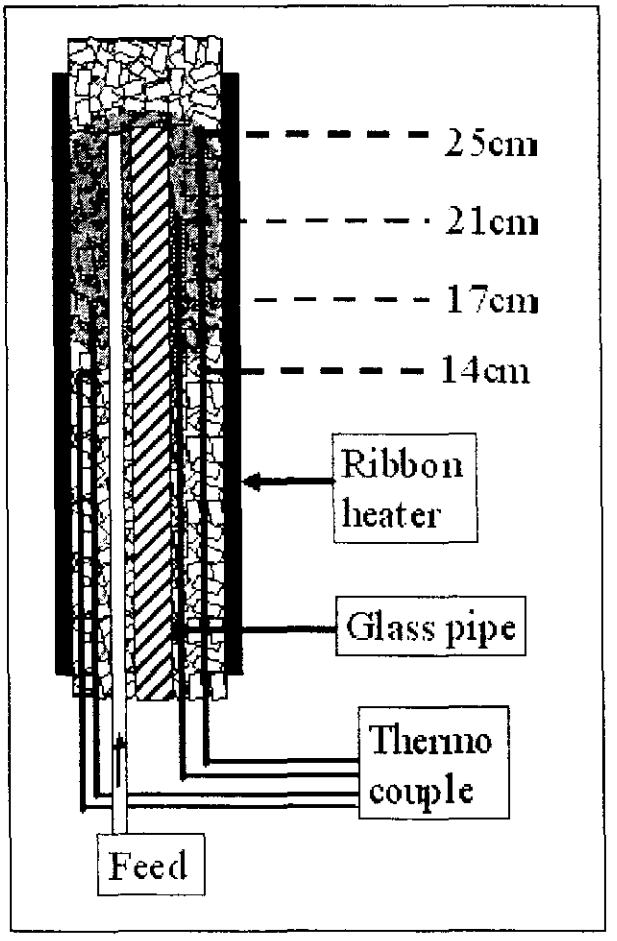

Figure 3. Details of the Reaction Part

The upper part of the column packed with 90 g of stainless-steel mesh saddles (48 mesh; 3-mm in diameter, and 6-mm in length) functioned as the *distillation part.* The mesh saddles (a) increase the surface area of contact between vapor and liquid and (b) enhance the separation of acetone from 2–propanol. The top vapor product was totally condensed through a condenser at a temperature of –30°C. The concentrations of acetone and 2–propanol in the distillate were analyzed using a gas chromatograph. Hence, the mole fraction of acetone in the distillate can be determined.

From the stochiometric relation of Eq. (1), the conversion of 2–propanol, X_A corresponds to the mole fraction of acetone in the distillate.

RESULTS AND DISCUSSIONS

Preliminary experiments with batch reactor

To check the effect of liquid volume on the conversion, the mole fraction of 2–propanol was measured by using a batch reactor. The liquid volumes were varied from 20 to 75 cm^3 in a batch reactor packed with 30 g of Ru-Pt/C as can be seen in Figure 4.

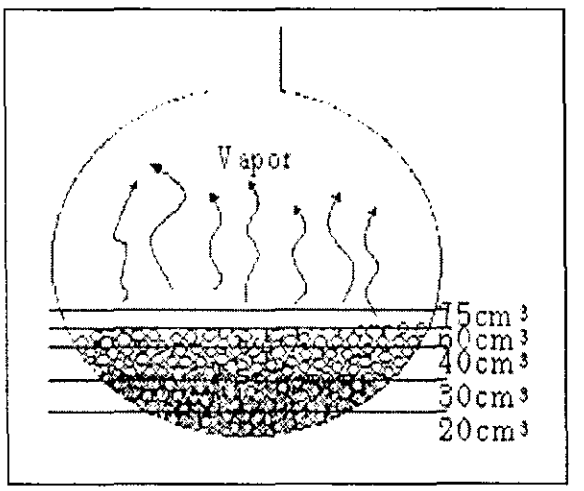

Figure 4. Position of Liquid Level Ru-Pt/C

Figure 5 shows the effects of liquid volume on the conversion. The conversion has a maximum value of 30 cm^3 which, as can be noted from the liquid level in Figure 4, is a partially wetted condition. This condition may be repeated between wet and dry states.

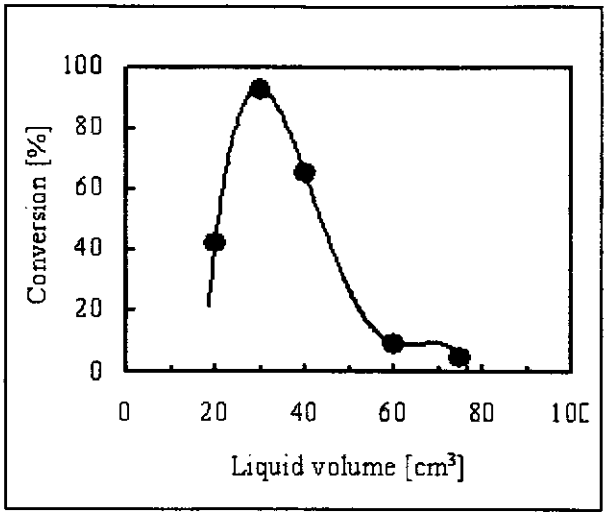

Figure 5. Effect of Liquid Volume on Conversion in a Batch Reactor

Experiments with periodic operation

Figure 6 plots the effect of periodic operation on the conversion. Note that with periodic operation, conversion increases. This effect reaches its optimum at a pulse interval of 3 min. Therefore, in periodic operation, the wet and dry states around the catalyst are suitable at a pulse interval of 3 min in this condition.

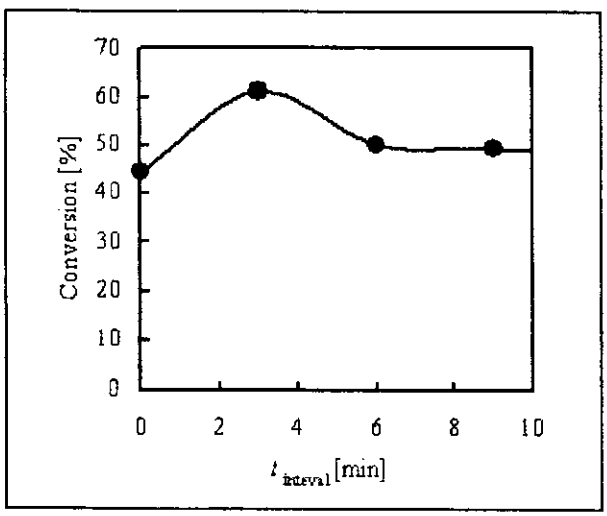

Figure 6. Effect of Pulse Interval on Conversion at T=90°C, Ru-Pt/C, and 62 μmol/s

Effect of reactive distillation

To check the effect of reactive distillation, experiments were conducted without the reactive distillation column.

Figure 7 shows the effect of periodic operation on the conversion. The effect is minimal without the distillation column as compared with that with the distillation column (see Fig. 6).

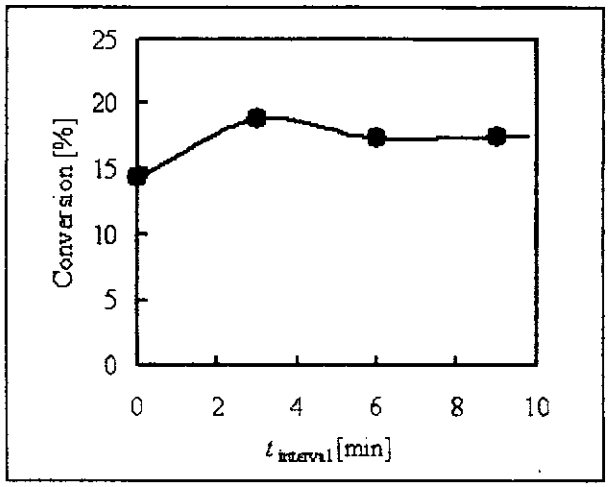

Figure 7. Effect of Pulse Interval on Conversion at T = 110°C, Ru-Pt/C, and 62 μmol/s Without Reactive Distillation

Temperature profiles in reaction part

Figure 8 shows the temperature profiles in the reaction part without periodic operation; that is, in steady state. At each position (refer to Fig. 3), the temperature remains constant below the boiling point of 2-propanol (82.4°C). This trend means that the solid catalyst is always wet.

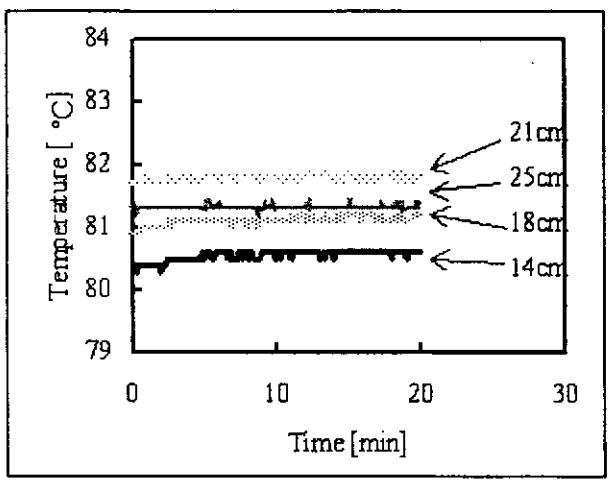

Figure 8. Temperature Profile in the Reaction Part at T=110°C, Ru-Pt/C, and 62μmol/s, Steady-State Operation Without Reactive Distillation

Figure 9 shows the temperature profiles in the reaction part at a pulse interval of 9 min. Although the temperatures are almost stable, the temperature at 14 cm is significantly variable. The peak is higher than the boiling point of 2-propanol. This trend means that the solid catalyst is periodically dry, a state which causes a higher reaction rate.

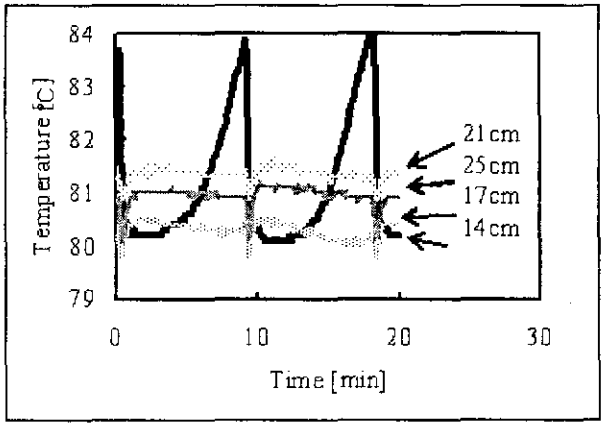

Figure 9. Temperature Profile in the Reaction Part at T=110°C, Ru-Pt/C, and 62μmol/s, 9-min Pulse Interval Without Reactive Distillation

Mass balance

Figure 10 shows a mass balance between input and output. At each experimental condition, the mass balance is in the range of 80 to 100 %.

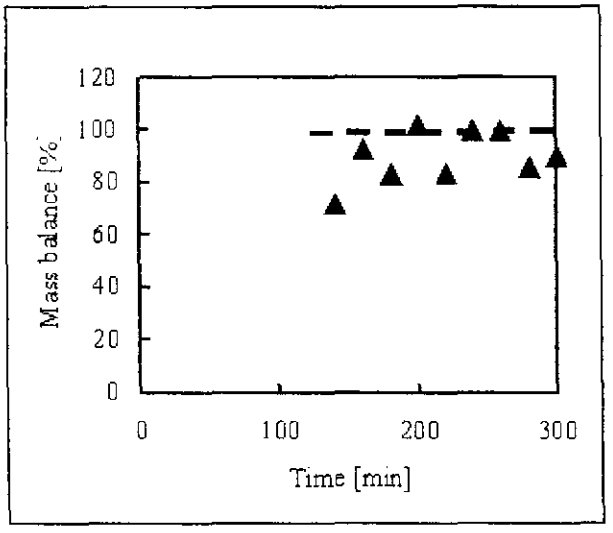

Figure 10. Temperature Course of Mass Balance at T=110°C, Ru-Pt/C, and 62μmol/s, 3-min Pulse Interval

Effect of Ru-Pd/C catalyst

Figure 11 shows the effect of periodic operation on the conversion using Ru-Pd/C catalyst at 62 mmol/s. This catalyst exhibited similar tendencies with the Ru-Pt/C catalyst. The optimum value is seen at a pulse interval of 3 min.

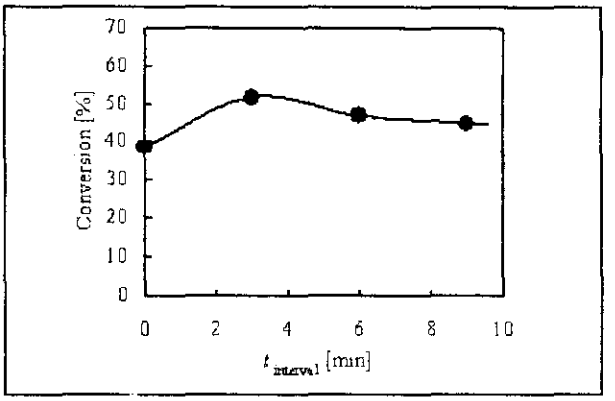

Figure 11. Effect of Pulse Interval on Conversion at T=110°C, Ru-Pt/C, and 62μmol/s

Figure 12 shows the same plot at a higher feed rate at 87 mmol/s. The maximum conversion goes higher at a pulse interval of 9 min.

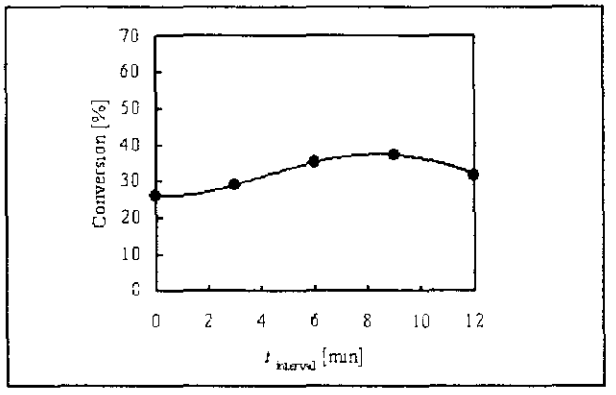

Figure 12. Effect of Pulse Interval on Conversion at T=110°C, Ru-Pt/C, and 87 μmol/s

The enhancement ratio of periodic operation

The *enhancement ratio* of periodic operation, g_A is defined as follows:

$$g_A = (X_{A,periodic} - X_{A,steady}) / X_{A,steady} \quad (2)$$

Figure 13 shows the enhancement ratios of periodic operation, g_A at Ru-Pt/C catalyst. The conversions attaim maximum values at a pulse interval 3 min for cases both with and without reactive distillation. The periodic operation results in a 30–40% increase in the conversion.

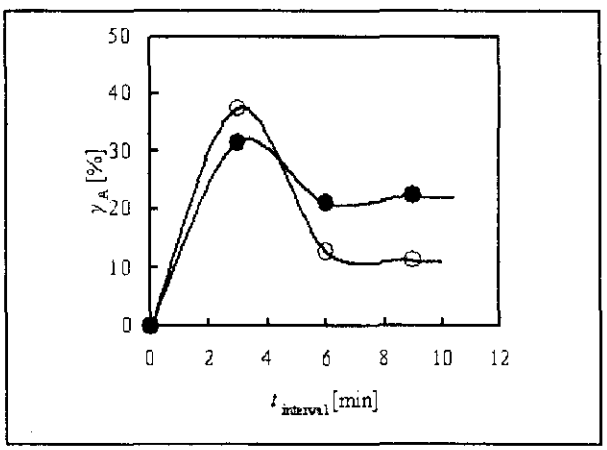

Figure 13. Effect of Pulse Interval on the Enhancement Ratio at Ru-Pt/C and 62μmol/s

Figure 14 shows the enhancement ratio of periodic operation, g_A at Ru-Pd/C catalyst. When the feed rate increases, the optimized pulse interval is varied from 3 to 9 min. An increased of 35-45% conversion is achieved.

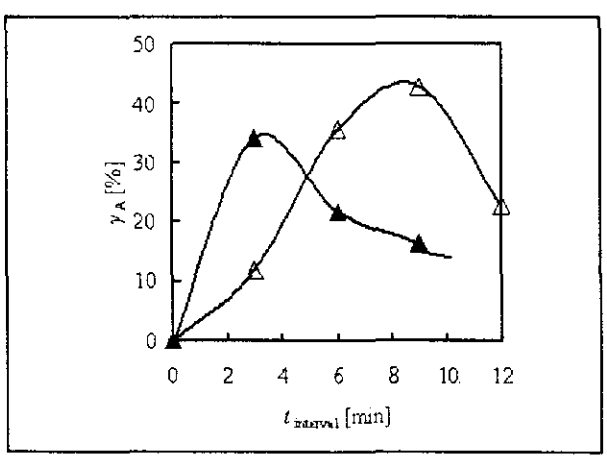

Figure 14. Effect of Pulse Interval on the Enhancement Ratio at Ru-Pt/C

CONCLUSION

The dehydrogenation of 2-propanol to produce acetone and hydrogen was investigated by using a reactive distillation column with periodic operation. This experimental condition of periodic operation resulted in a 30 to 40 % higher reaction rate than that in steady-state operation. Periodic operation, therefore, is effective for the dehydrogenation of 2-propanol in a reactive distillation column.

ACKNOWLEDGMENT

The authors are deeply indebted to Miss S. Fukai for her experimental help and to Mr. H. Itoh for his technical advice.

NOMENCLATURE

T	temperature	K
$t_{interval}$	pulse interval	s
X_A	conversion	
g_A	enhancement ratio of periodic operation	

REFERENCES

Gaspillo, P. D., Abella, L. C., and Goto, S. (1998). "Dehydrogenation of 2-propanol in reactive distillation column for chemical heat pump," *J. Chem. Eng. Japan, 31,* 3, 440–44.

Gastauer, P., and Prevost, M. (1993). "Dehydrogenation of isopropanol at low temperatures in the vapor phase as a reaction for a chemical heat pump," *J. Chem. Eng. Japan, 26,* 5, 580–83.

Ito, E., Yamashita, M., Hagiwara, S., and Saito, Y. (1991). "A composite Ru-Pt catalyst for 2-propanol dehydrogenation adoptable to the chemical heat pump system," *Chemistry Letters,* 351–54.

Kim, T. G., Yeo, Y. K., and Song, H. K. (1992). "Chemical heat pump-based on dehydrogenation and hydrogenation of *i*-propanol and acetone," *Inter. J. Energy Research, 16,* 897–916.

Kobayashi, I., Yamamoto, K., and Kameyama, H. (1999). "A Proposal of a spray-pulse operation for liquid film dehydrogenation—2-propanol dehydrogenation on a plate catalyst," *Chem. Eng. Sci., 54,* 10, 1319–23.

Saito, Y. (1995). "The properties of liquid film-type dehydrogenation catalytic reaction," *Hyomen, 33,* 1, 1–9.

Saito, Y., Kameyama, H., and Yoshida, K. (1987). "Catalyst-assisted chemical heat with reaction couple of acetone hydrogenation/2–propanol dehydrogenation for upgrading low-level thermal energy: Proposal and evaluation," *Inter. J. Energy Research, 11,* 549–58.

Taneda, D., Yasutomi, I., Shibata, S., and Toida, T. (1993). "Studies of 2–propanol/acetone/hydrogen chemical heat pump characteristics," *Kagaku Kogaku Ronbunshu, 19,* 5, 729–35.